

Application Note 524[†]

Analysis of complex petrochemicals by GC×GC–TOF MS with Select-eV variable-energy electron ionisation

Summary

This Application Note shows that BenchTOF instruments, coupled with GC×GC, can provide a high-performance solution for the characterisation of hydrocarbons in complex petrochemical samples. Variable-energy electron ionisation technology is also shown to enhance analyte speciation by providing additional data on both molecular ions and structurally significant fragments in the low-energy mass spectra. The enhanced sensitivity and selectivity stemming from the dramatic reduction in fragmentation at low energies also greatly increases the number of compounds identified, permitting robust statistical comparisons essential for successful chemical fingerprinting.



Introduction

Crude oil contains thousands of organic compounds ranging from light hydrocarbons to complex biomolecules. Speciation of hydrocarbons is of great interest to the petroleum industry, as certain isomers may have an adverse effect on engine performance if present in high quantities in the final fuel. Furthermore, chemical fingerprinting of crude oil has become extremely important for identification of those responsible for environmental contamination events.

In the past, such complex samples were analysed by chemical fractionation followed by one-dimensional gas chromatography with mass spectrometry (GC–MS). However, fractionation is a time-consuming, labour-intensive process, which uses large volumes of solvents and can be prone to error.

Two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC–TOF MS) is now used routinely in the oil industry to combat this problem. The coupling of two columns of different selectivity provides

enhanced separation of complex mixtures, allowing all chemical classes to be monitored in a single analytical run.

Despite the superior separation afforded by GC×GC, the identification of individual compounds in complex samples remains challenging when multiple compounds in a chemical class have similar spectra at conventional (70 eV) ionisation energies. Branched alkanes are a prime example, with weak molecular ions that further complicate the process. Spectral similarity can be addressed by the use of soft ionisation to reduce the degree of ion fragmentation, but this approach has been cumbersome to implement until now.

In this Application Note, we show how the problem of compound identification in petrochemical samples can be resolved without recourse to the time-consuming analysis of multiple standards. We achieve this by the application of Select-eV, a revolutionary MS source technology that enhances compound identification by enabling efficient electron ionisation at much lower (softer) energies without compromising sensitivity. We also show how Select-eV complements the other fundamental advantages of Markes' BenchTOF time-of-flight mass spectrometers for the GC×GC identification of hydrocarbons.

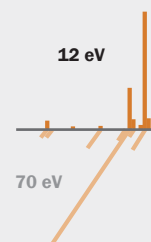


Select-eV

Markes' flagship BenchTOF-Select™ instrument features Select-eV® ion-source technology as standard.

Select-eV breaks new ground by allowing ionisation energies to be reduced on a sliding scale from 70 eV to 10 eV, without impacting sensitivity, simply by changing a parameter in the method.

This low-energy (*i.e.* 'soft') electron ionisation reduces analyte fragmentation, which benefits a wide range of GC and GC×GC analyses by enhancing selectivity, sensitivity, and aiding structural elucidation – all while avoiding the inconvenience of reagent gases, ion source pressurisation, or changes in hardware setup typically associated with other soft ionisation techniques for GC–MS.



[†] Formerly ALMSCO Application Note 024.



Background to BenchTOF instruments

Markes' BenchTOF™ time-of-flight mass spectrometers are designed specifically for gas chromatography. They are particularly appropriate for the GC×GC analysis of complex samples, such as petrochemicals, because they offer exceptional sensitivity, spectral quality and speed:

- **Sensitivity:** Highly efficient direct-extraction technology allows BenchTOF instruments to acquire full-range spectra with SIM-like sensitivity, allowing them to reliably detect trace-level analytes in a single run, which would be difficult or impossible on a quadrupole system.
- **Spectral quality:** The 'reference-quality' spectra produced by BenchTOF instruments are a close match for those in commercial libraries such as NIST or Wiley. This enables quick and confident matching of both targets and unknowns.
- **Speed:** The ability to record full-range mass spectral information to extremely high densities (10,000 transient spectral accumulations per second) enables BenchTOF to handle the narrowest peaks encountered in well-optimised GC×GC couplings. The high stored-to-disk data rate also enables advanced spectral deconvolution and 'data-mining' algorithms to extract maximum information from weak, matrix-masked signals.

Experimental

GC×GC separations were conducted using a conventional apolar–polar column set, using a 100 mg/mL dilution of crude oil in dichloromethane.

GC:

Instrument: Agilent 7890A
Injector: Split/splitless injector
Liner: 4.0 mm i.d. liner, 1 µL injection
Carrier gas: He, constant flow at 1.0 mL/min Split, 100:1
Mode: 280 °C
Temperature: 280 °C
Septum purge: On, 3 mL/min

2D column set:

1st dimension: DB-5, 28 m × 0.25 mm × 0.25 µm SGE
2nd dimension: BPX50, 3.3 m × 0.1 mm × 0.1 µm As for 2nd dimension
Modulation loop: Equivalent pneumatic impedance to 41.5 m × 0.18 mm (calculated from K factor look-up charts for 1st- and 2nd-dimension columns used)

Temperature programme:

Main oven: 50 °C (1.0 min), 4.0 °C/min to 325 °C (10 min)
Secondary oven: 75 °C (1.0 min), 4.2 °C/min to 340 °C (hold time matched to total run time)
Hot jet: 150 °C (1.0 min), 4.0 °C/min to 400 °C (hold time matched to total run time)
Cold jet: Modulation period: Total run time: Dewar fill: high, 50%; low, 40%
6 s, hot-jet pulse 350 ms
79.75 min

TOF MS:

Instrument: BenchTOF-Select (Markes International)
Filament voltage: 2.2 V
Ion source: Transfer 250 °C
line: Mass range: 325 °C
Data rate: m/z 40–600
50 Hz (200 spectral accumulations per data point)

Software:

Image processing: GC Image™ (GC Image, LLC)





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